

## INTERNATIONAL APPLICATION PUBLISHED PURSUANT TO THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification<sup>6</sup>:</b> A61K 7/06, 7/48	<b>A1</b>	<b>(11) International Publication No.:</b> WO 98/00096 <b>(43) International Publication Date:</b> January 8, 1998 (1/8/98)
<b>(21) International Application No.:</b> PCT/FR97/01165 <b>(22) International Filing Date:</b> June 30, 1997 (6/30/97) <b>(30) Priority information:</b> 96/08220 July 2, 1996 (7/2/96) FR <b>(71) Applicant: (for all treaty states except the US):</b> L'OREAL [FR/FR]; 14, rue Royale, F-75008 Paris (FR). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> MONDET, Jean [FR/FR]; 90, rue Roger-Lemaire, F-93600 Aulnay-sous-Bois (FR). LION, Bertrand [FR/FR]; 2, rue Denis Papin, F-93190 Livry Gargan (FR). <b>(74) Agent:</b> MISZPUTEN, Laurent; L'Oréal - D.P.I., 90, rue du Général-Roguet, F-92583 Clichy Cédex (FR).		<b>(81) Designated countries:</b> JP, US, European Patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With International Search Report.</i> <i>Prior to expiration of the time allowed for amendment of claims. Publication will be repeated if amendments are received.</i>
<b>(54) Title:</b> USE OF ACRYLIC COPOLYMERS IN COSMETICS, AND COMPOSITIONS USED  <b>(57) [Original English] Abstract:</b>  The invention discloses the use in and for the preparation of cosmetic and dermatological composition of one copolymer obtainable by the copolymerisation of a mixture of monomers comprising: (a) 5 to 25 wt.% of at least one ethylenically unsaturated monomer (A) comprising at least one carboxylic acid function; (b) 3 to 30 wt.% of at least one monomer (B) of formula (I): $H_2C-C(R_1)-COOR_2$ in which $R_1$ represents a hydrogen atom or a methyl radical; $R_2$ represents a linear or branched or cyclic, saturated or unsaturated or aromatic alkyl radical, having 8 to 40 carbon atoms; (c) of at least one monomer (C) selected from the group constituted by tertio-butyl methacrylate, tertio-butyl acrylate and their mixtures, in a proportion higher than 50%, such that the polymer glass transition temperature ( $T_g$ ) is at least 15° C, the weight percentages being computed with respect to the total amount of monomer used. The invention also concerns the cosmetic and dermatological compositions used.		

*FOR INFORMATION ONLY*

Codes used to identify the PCT member nations on the cover pages of the pamphlets publishing International Applications pursuant to the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia-Herzegovina	GE	Georgia	MD	Moldova Republic	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	Former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Nigeria	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Vietnam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZM	Zimbabwe
CI	Ivory Coast	KP	Democratic Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Lichtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## USE OF ACRYLIC COPOLYMERS IN COSMETICS, AND COMPOSITIONS USED

The present invention concerns the use of acrylic copolymers in and for the preparation of cosmetic and dermatological preparations, as well as the compositions used.

5

For many cosmetic applications, especially those intended for treating and caring for the hair, skin, or eyelashes, polymers are used which are capable, after being applied onto the substrate to be treated and having dried, of forming a deposit having mechanical properties and adhesion properties. From this standpoint, polymers which can easily be eliminated when acted upon by an aqueous solution of surfactants are desirable. Concurrently, it is desirable to obtain a film-forming deposit which can resist ambient moisture, in particular a deposit which is non-hygroscopic to the touch, which resists rain (hair or skin applications), or which resists tear fluid (mascaras). Also desirable is a film-forming deposit for imparting cosmetic properties such as softness to the touch, which are generally conferred by hydrophobic substances in cosmetics.

10

15

Another problem relating to deposited polymers arises in the field of hair care, in particular in the context of products for holding or setting the hair. Specifically, it is often difficult to adapt the properties of the polymer that is to be deposited to yield simultaneously good setting of the hairdo, good holding of that set, and easy elimination by combing or brushing.

20

It is known to use acrylic copolymers in cosmetic compositions. For example, JP patent application A-87-167307 describes a hair styling polymer obtained by copolymerization of the monomer mixture comprising:

25

- (i) 10 to 50% by weight unsaturated carboxylic acids;
- (ii) 10 to 70% by weight esters of acrylic acid and/or of methacrylic acid;
- (iii) 0 to 50% vinyl monomers.

With this polymer, it is possible to impart good smoothness to the hair while maintaining a good feel. The presence of the fatty chain in the polymer, however, contributed by the acrylic acid and/or methacrylic acid esters, makes it difficult to eliminate the polymer that has set onto the hair.

Also disclosed, by JP application A-08092046, is a cosmetic hair-care composition containing a copolymer comprising 6 to 35% by weight (meth)acrylic acid or itaconic acid, 15 to 50% by weight  $C_{10}$  through  $C_{18}$  alkyl (meth)acrylate, 15 to 50% by weight  $C_4$  through  $C_8$  alkyl (meth)acrylate, and 0 to 25% of a vinyl-type, in particular acrylamide, monomer. These polymers are difficult to use in compositions comprising an alcohol medium, however, those compositions being particularly advantageous because of their reduced drying time.

One of the purposes of the present invention is thus to use, in cosmetic or dermatological compositions, acrylic polymers which have satisfactory adhesion and mechanical properties and film-forming properties, which can easily be eliminated when acted upon by an aqueous solution of surfactants, and which can easily be incorporated into compositions comprising at least an alcohol medium. In addition, a goal of the invention is to use film-forming polymers which afford good cosmetic properties before and after elimination of the composition.

Another purpose of the invention is to use, in and for the preparation of hair styling compositions, polymers which have both substantial setting characteristics which readily withstand weak stresses, and good rigidity, and are then eliminated very easily by shampooing, brushing, or combing, while

affording good cosmetic properties such as softness to the touch. In particular, one of the purposes of the invention is to propose the use of polymers which are easy to utilize in hair-care compositions comprising an alcohol medium to allow rapid drying of the composition, said composition having good fixing ability without tackiness.

The Applicant has discovered, surprisingly, that these purposes could be achieved by using particular acrylic copolymers in and for the preparation of cosmetic or dermatological preparations.

The object of the present invention is the use, in and for the preparation of cosmetic or dermatological compositions, of a copolymer capable of being produced by copolymerization of a mixture of monomers comprising:

(a) 5 to 25% by weight of at least one ethylene-unsaturated monomer (A) having at least one carboxylic acid group;

(b) 3 to 30% by weight of at least one monomer (B) having the formula (I):



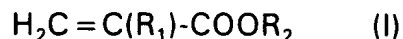
in which

- $\text{R}_1$  designates a hydrogen atom or a methyl radical; and
  - $\text{R}_2$  designates a linear, branched or cyclic, saturated, unsaturated or aromatic alkyl radical having 8 to 40 carbon atoms;
  - (c) at least one monomer (C) selected from the group constituted by tert-butyl methacrylate, tert-butyl acrylate, and their mixtures, in a proportion at least greater than 50% by weight, such that the glass transition temperature ( $T_g$ ) of the polymer is greater than or equal to  $15^\circ\text{C}$ ;
- the percentages by weight being calculated in terms of the total quantity of monomers used.

The present invention also concerns cosmetic or dermatological compositions containing, in a cosmetically or dermatologically acceptable medium, at least one copolymer produced by copolymerization of:

(a) 5 to 25% by weight of at least one ethylene-unsaturated monomer (A) having at least one carboxylic acid group;

(b) 3 to 30% by weight of at least one monomer (B) having the formula (I):



in which

- $\text{R}_1$  designates a hydrogen atom or a methyl radical; and
- $\text{R}_2$  designates a linear, branched or cyclic, saturated, unsaturated or aromatic alkyl radical having 8 to 40 carbon atoms;

(c) at least one monomer (C) selected from the group constituted by tert-butyl methacrylate, tert-butyl acrylate, and their mixtures, in a proportion at least greater than 50% by weight, such that the glass transition temperature ( $T_g$ ) of the polymer is greater than or equal to  $15^\circ\text{C}$ ;

the percentages by weight being calculated in terms of the total quantity of monomers used.

It has been found that the copolymer used according to the invention for hair-care compositions yields very good cosmetic properties, in particular a good feel and good elimination by either brushing or shampooing. In particular, after application of the composition, the hair exhibits a pleasant feel without creating a "board-like" effect, i.e. without imparting excessive stiffness to the hair. The composition thus exhibits good fixing ability, and after application to the hair, the resulting film has practically no tackiness. The copolymer according to the invention is moreover compatible with alcohol media and can thus easily be utilized in a composition having a reduced drying time.

Other objects will be apparent from the description and the examples below.

Preferably:

- the concentration of monomer (A) is 6 to 20% by weight, and more preferably 6 to 15% by weight;

- the concentration of monomer (B) is 5 to 25% by weight, and more preferably 13 to 22% by weight;
- the concentration of monomer (C) is 55 to 80% by weight, and more preferably 60 to 70% by weight.

5

The monomers (A) used to prepare the polymers according to the invention are selected, for example, from the group constituted by: the ethylene-unsaturated carboxylic monoacids such as acrylic acid, methacrylic acid, and crotonic acid; the ethylene-unsaturated carboxylic diacids such as maleic acid, fumaric acid, itaconic acid, and their monoester or monoamide derivatives having one C<sub>1</sub> - C<sub>4</sub> alkyl group; [and] allyloxyacetic acid. Acrylic acid, methacrylic acid, and mixtures thereof are more particularly used.

10

In the monomers (B), R<sub>2</sub> is preferably a linear or branched saturated alkyl radical having 8 to 40 carbon atoms, and preferably 8 to 30 carbon atoms. It can, in particular, be a radical corresponding to the Guerbet alcohols of the formula -CH<sub>2</sub>-CH(R<sub>3</sub>)(R<sub>4</sub>), in which R<sub>3</sub> and R<sub>4</sub>, identical or different, designate a linear or branched saturated alkyl radical, the total number of carbon atoms of R<sub>3</sub> and R<sub>4</sub> ranging from 6 to 38, and preferably from 6 to 28.

15

Advantageously, R<sub>2</sub> is selected from the group formed by lauryl, stearyl, and ethyl-2 hexyl radicals.

20

The copolymers used according to the invention preferably consist of a mixture of monomers (A), (B), and (C) as defined above.

25

The copolymers according to the invention preferably have an average molecular weight, measured at the top of the peak by steric exclusion chromatography, ranging from 5000 to 2,000,000, and in particular from 20,000 to 1,000,000.

Advantageously, the polymer according to the invention has a glass transition temperature ranging from 40°C to 90°C.

5 The copolymer according to the invention can be produced by radical copolymerization of the monomers as defined above.

Radical polymerization can be performed in solution in a solvent common to all the monomers used and to the polymer produced, or in a mixture of common solvents. Ethyl acetate or alcohol may be mentioned as solvents. The reaction is generally performed at a temperature ranging from 30°C to the boiling  
10 temperature of the solvent used. Polymerization can also be performed in a heterogeneous medium, in particular in suspension, by precipitation, or in emulsion.

Radical polymerization can be initiated by a conventional organic initiator, for  
15 example azobis-N-butyronitrile, bis(2-ethylhexyl) peroxydicarbonate, or tert-butyl peroxy-2-ethylhexanoate.

When polymerization is performed in emulsion, it is also possible to use a water-soluble thermal initiator such as potassium persulfate, hydrogen peroxide, or a water-soluble redox system, for example of the persulfate/metabisulfite  
20 type. In addition, stabilization of the emulsion is accomplished in known fashion by way of a surfactant or a mixture of surfactants, the most commonly used being sodium lauryl sulfate or the alkyl ethoxysulfates.

The duration of the polymerization reaction can range, in general, from 4 hours  
25 to 18 hours.

Advantageously, the copolymer according to the invention can be partially or totally neutralized depending on the desired solubility of the polymer in the composition. The neutralization level can range, in particular, from 30% to  
30 100%. Neutralization can be accomplished using an organic or mineral base.



Caustic soda or potash may be mentioned as the mineral base. An aminoalcohol taken from the group constituted by 2-amino-2-methyl-1-propanol (AMP), triethanolamine, triisopropanolamine (TIPA), monoethanolamine, diethanolamine, tri[(2-hydroxy)-1-propyl]amine, 2-amino-2-methyl-1,3-propanediol (AMPD), and 2-amino-2-(hydroxymethyl)-1,3-propanediol, may be mentioned as the organic base.

The compositions according to the invention may also optionally contain a plasticizing agent to improve the mechanical properties, cosmetic properties, and adhesion to keratinaceous materials of the film-forming acrylic that is deposited, after application and drying. The presence of a plasticizing agent is not mandatory to adjust the fixing ability in hair spray formulations according to the invention, in contrast to conventional hair spray formulations.

Among the plasticizing agents that can be used according to the invention may be mentioned:

- the CARBITOLS of the UNION CARBIDE company, specifically CARBITOL or diethylene glycol ethyl ether, methyl CARBITOL or diethylene glycol methyl ether, butyl CARBITOL or diethylene glycol butyl ether, or hexyl CARBITOL or diethylene glycol hexyl ether;
- the CELLOSOLVES of the UNION CARBIDE company, specifically CELLOSOLVE or ethylene glycol ethyl ether, butyl CELLOSOLVE or ethylene glycol butyl ether, hexyl CELLOSOLVE or ethylene glycol hexyl ether;
- the derivatives of propylene glycol, and in particular propylene glycol phenyl ether, propylene glycol diacetate, dipropylene glycol butyl ether, tripropylene glycol butyl ether, as well as the DOWANOLS of the DOW CHEMICAL company, specifically DOWANOL PM or propylene glycol methyl ether, DOWANOL DPM or dipropylene glycol methyl ether, and DOWANOL TPM or tripropylene glycol methyl ether.

The following may also be mentioned:

- diethylene glycol methyl ether or DOWANOL DM of the DOW CHEMICAL company;
- ethoxylated castor oil with 40 moles of ethylene oxide, such as that sold by the RHÔNE POULENC company under the name "MULGOFEN LE-719";
- benzyl alcohol;
- the triethyl citrate sold by the PFIZER company under the name ;
- 1,3-butylene glycol;
- diethyl, dibutyl, and diisopropyl phthalates and adipates;
- diethyl and dibutyl tartrates;
- diethyl-, dibutyl-, and diethyl-2-hexyl phosphates; and
- glycerol esters such as glycerol diacetate (diacetin) and glycerol triacetate (triacetin).

The plasticizers are selected more particularly from among those which are hydrophilic or water-soluble.

The plasticizing agent is present in a proportion ranging, preferably, from 0 to 20% by weight in terms of the weight of the film-forming polymer. This proportion varies depending on the application being considered.

The cosmetic and dermatological compositions according to the invention thus contain, in a cosmetically or dermatologically acceptable substrate, the polymers such as those described above, for applications as varied as those encountered, for example, in the field of hair care, makeup, or also for skin care, or any other cosmetic field in which the use of a film-forming substance is desirable.

The copolymers according to the invention can be used alone as the film-forming agent or also as an additive to conventional film-forming agents in and for the preparation of cosmetic or dermatological compositions.

Among the applications for which the present invention is preferably intended, the following may be more particularly mentioned:

- The field of hair-care products (for washing, caring for, or beautifying the hair), in which the compositions according to the invention may occur in the form of aerosols, mousse, shampoos, after-shampoo preparations, styling or treating lotions or gels, hair sprays or shaping or waving or setting lotions.
- The field of makeup products, in particular for making up the nails, eyelashes, or lips, in which the compositions according to the invention may occur in the form of nail polishes; mascaras or eyeliners; or lipsticks.
- The field of skin-care products (cremes, milks, lotions, masks, serums, solar products).

The copolymer is present in the cosmetic or dermatological compositions according to the invention at a concentration ranging generally from 0.1 to 50%, and more preferably from 1 to 30%, by weight in terms of the total weight of the composition. It varies depending on the cosmetic or dermatological application being considered.

In the case of hair-care composition, the polymer concentration can range from 0.5 to 25%, and in particular from 1 to 20%, by weight in terms of the total weight of the composition.

In the case of nail polishes, said proportion ranges generally from 2 to 35% by weight, and when the copolymer according to the invention is used alone as the film-forming agent, the concentration is equal to or greater than 30% by weight in terms of the total weight of the composition.

In the case of mascaras or eyeliners, the polymer concentration generally ranges from 1 to 30% by weight in terms of the total weight of the composition.

5 In the case of skin-care compositions, the polymer concentration ranges from 0.5 to 20% by weight in terms of the total weight of the composition.

10 The cosmetically acceptable substrate of the compositions according to the invention is preferably constituted by water, by one or more cosmetically acceptable organic solvents, or by a mixture of water and one or more cosmetically acceptable organic solvents.

Among the organic solvents, the  $C_1 - C_4$  lower alcohols, such as ethanol, are more particularly used.

15 The copolymers according to the invention are dissolved or in dispersion in the substrate of the compositions according to the invention.

20 The compositions can also, of course, contain various adjuvants intended to make them acceptable for a particular cosmetic application.

25 The compositions according to the invention may contain conventional cosmetic additives selected from among the fats such as mineral, vegetable, animal, or synthetic oils; animal, fossil, vegetable, mineral, or synthetic waxes; organic solvents; thickening agents; softeners; antifoaming agents; moisturizing agents; humectants; processing agents (anti-slumping, anti-skinning, etc. agents); antiperspirants; alkalizing agents; UV-A or UV-B or broad-spectrum solar filters; coloring agents; pigments; perfumes; plasticizers; preservatives; anionic,

nonionic, or amphoteric organic polymers, that are compatible with the copolymers according to the invention, and propellants when the compositions are present in aerosol form.

Those skilled in the art will of course take care to select any complementary compound or compounds mentioned above in such a way that the advantageous properties attached intrinsically to the compositions according to the invention are not, or are not substantially, altered by the additives that are considered.

Another object of the invention is a method for cosmetic treatment of keratinaceous materials such as the skin, hair, scalp, eyelashes, eyebrows, nails, and lips, characterized by consisting in applying onto the latter a composition such as that defined above.

The examples below serve to illustrate the invention, but are not limiting in nature.

#### **EXAMPLES 1 THROUGH 5 – PREPARATION**

**Example 1:** Preparation of a copolymer produced from a mixture constituted by:

- 15% by weight acrylic acid
- 65% by weight tert-butyl acrylate
- 20% by weight lauryl acrylate

15 g acrylic acid, 65 g tert-butyl acrylate, and 20 g lauryl acrylate were introduced in succession into a reactor under a flow of nitrogen. 200 g ethyl acetate, and 2 ml of the tert-butyl peroxy-2-ethylhexanoate initiator sold under the name "Trigonox 21 S" by the AKZO company, were then added. Stirring was applied at ambient temperature to produce a homogeneous mixture. The mixture was then heated for 12 hours, with reflux of the ethyl

acetate, to achieve polymerization. The reaction medium was then diluted by adding 100 g ethyl acetate, and was then cooled to ambient temperature.

The reaction solution was purified by precipitation in 8 liters of petroleum ether.

The precipitated polymer that was obtained was dried in an oven. Ninety-one grams of polymer was obtained, having the following characteristics:

Acid index: 137.5

$T_g = 44^{\circ}\text{C}$

The molecular weight was characterized by steric exclusion chromatography on a microstyragel column eluted with tetrahydrofuran. The results are expressed with reference to a polystyrene control.

The polymer obtained yielded a principal peak corresponding to a molecular weight of 322,000, and a shoulder toward high molecular weights corresponding to a molecular weight of 1,308,000.

**Example 2:** Preparation of a copolymer produced from a mixture constituted by:

- 15% by weight acrylic acid
- 70% by weight tert-butyl acrylate
- 15% by weight stearyl methacrylate

The polymer was prepared under the same operating conditions as for Example 1.

90 g of polymer was obtained, having the following characteristics:

Acid index: 130

$T_g = 53^{\circ}\text{C}$

Molecular weight: - Principal peak: MW = 182,000

- Shoulder: 1,030,000

**Example 3:** Preparation of a copolymer produced from a mixture constituted by:

- 15% by weight acrylic acid
- 70% by weight tert-butyl acrylate
- 15% by weight stearyl acrylate

5 The polymer was prepared under the same operating conditions as for Example 1.

90 g of polymer was obtained, having the following characteristics:

Acid index: 129

T<sub>g</sub> = 52°C

10 Molecular weight: - Principal peak: MW = 160,000; no shoulder

**Example 4:** Preparation of a copolymer produced from a mixture constituted by:

- 15% by weight acrylic acid
- 15 - 65% by weight tert-butyl acrylate
- 20% by weight lauryl acrylate

The polymer was prepared under the same operating conditions as for Example 1, replacing the ethyl acetate with ethanol.

20 80 g of polymer was obtained, having the following characteristics:

Acid index: 139.5

T<sub>g</sub> = 44°C

Molecular weight: - Principal peak: MW = 96,000; no shoulder

25 **Example 5:** Preparation of a copolymer produced from a mixture constituted by:

- 20% by weight acrylic acid
- 60% by weight tert-butyl acrylate
- 30 - 20% by weight ethyl-2-hexyl acrylate

The polymer was prepared under the same operating conditions as for Example 4, using only 1 ml of initiator.

80 g of polymer was obtained, having the following characteristics:

Acid index: 161

Molecular weight: - Principal peak: MW = 113,000; no shoulder

5                                    **EXAMPLES 6 THROUGH 12 – COMPOSITION**

**Example 6:** Aerosol hair styling spray

**Composition A**

- 10            - Copolymer of Example 1                    2 g
- 2-amino-2-methyl-1-propanol            q.s. for 100% neutralization
- Ethanol                                        to make 100 g

15            An aerosol hair spray was prepared by packaging, in a suitable aerosol container:

- Composition A                                65 g
- Dimethyl ether                                35 g

20            The valve was attached, and the container was hermetically sealed. The spray applied onto the hair possessed good setting ability and good hold. The polymer film was easy to eliminate by brushing. The hair exhibited a good feel, even after brushing.

**Example 7:** Aerosol hair styling spray

25

**Composition B**

- Copolymer of Example 2                    2 g
- 2-amino-2-methyl-1-propanol            q.s. for 100% neutralization
- Ethanol                                        to make 100 g

30            An aerosol hair spray was prepared by packaging, in a suitable aerosol container:



- Composition B 65 g
- Dimethyl ether 35 g

The valve was attached, and the container was hermetically sealed. The spray applied onto the hair possessed good setting ability and good hold. The polymer film was easy to eliminate by brushing. The hair exhibited a good feel, even after brushing.

**Example 8:** Aerosol hair styling spray

**Composition C**

- Copolymer of Example 3 2 g
- 2-amino-2-methyl-1-propanol q.s. for 100% neutralization
- Ethanol to make 100 g

An aerosol hair spray was prepared by packaging, in a suitable aerosol container:

- Composition C 65 g
- Dimethyl ether 35 g

The valve was attached, and the container was hermetically sealed. The spray applied onto the hair possessed good setting ability and good hold. The polymer film was easy to eliminate by brushing. The hair exhibited a good feel, even after brushing.

**Example 9:** Aerosol hair styling spray

**Composition D**

- Copolymer of Example 5 8.6 g
- 2-amino-2-methyl-1-propanol q.s. for 50% neutralization
- Ethanol to make 100 g

An aerosol hair spray was prepared by packaging, in a suitable aerosol container:

- Composition D 37 g
- Dimethyl ether 43 g
- Pentane 20 g

The valve was attached, and the container was hermetically sealed. The spray applied onto the hair possessed good setting ability and good hold, with no cosmetic shortcomings such as powdering or tackiness. The polymer film was easy to eliminate by brushing. The hair exhibited a good feel, even after brushing.

**Example 10:** Aerosol hair styling spray

**Composition E**

- Copolymer of Example 4 8.6 g
- 2-amino-2-methyl-1-propanol q.s. for 50% neutralization
- Ethanol to make 100 g

An aerosol hair spray was prepared by packaging, in a suitable aerosol container:

- Composition E 37 g
- Dimethyl ether 43 g
- Pentane 20 g

The valve was attached, and the container was hermetically sealed. The spray applied onto the hair possessed good setting ability and good hold, with no cosmetic shortcomings such as powdering or tackiness. The polymer film was easy to eliminate by brushing. The hair exhibited a good feel, even after brushing.

**Example 11:** Mascara

## 1) Preparation of an aqueous dispersion of the polymer of Example 4:

- 5        30 g of the polymer of Example 4 was added to a solution of 90 g methyl ethyl ketone and 1.76 g 2-amino-2-methyl-1-propanol (quantity corresponding to 30% neutralization based on the acid index). After stirring at ambient temperature for 30 minutes, the polymer had completely dissolved.
- 10       An aqueous phase consisting of 120 g deionized water was added to the resulting organic phase, while stirring with an Ultra-Turrax disperser at 2000 rpm, to produce the emulsion.
- 15       When addition of the aqueous phase was complete, stirring was continued for 10-15 minutes at ambient temperature, allowing a translucent and stable emulsion to be obtained.
- Concentration was then performed using a rotary evaporator under partial vacuum at a temperature less than 50°C. After elimination of the methyl ethyl ketone, a stable dispersion was obtained with a polymer concentration of 20% by weight in terms of the total weight of the composition.
- 20       Particle size was measured by quasi-elastic light diffusion using a Coulter M4 instrument, and yielded the following results:
- Particle size:    45 nm
- Size polydispersity: 0.26

## 2) Preparation of the mascara:

Part A

5	-	Triethanolamine stearate	12 g
	-	Beeswax	6 g
	-	Carnauba wax	1 g
	-	Paraffin wax	3.5 g

Part B

10	-	Iron oxides	6 g
----	---	-------------	-----

Part C

15	-	Hydroxyethyl cellulose	
		("Cellosize QP" of Amerchol)	1 g
	-	Gum arabic	2 g
	-	Keratin hydrolysate	1.8 g

Part D

20	-	Aqueous dispersion of the polymer of Example 4	5 g
	-	Preservatives	q.s.
	-	Water	to make 100 g

This mascara was produced by heating the ingredients of part A to 85°C, adding part B to them, and stirring with a turbomixer.

25 The water for preparation was then boiled, the preservatives were added, and then the ingredients of part C were added at 85°C.

The resulting aqueous phase was then added to part A while stirring with a turbomixer, then the aqueous polymer dispersion of part D was added, and the mixture was stirred with a paddle mixer.

**Example 12:** Nail care

A nail care base having the following composition was prepared:

5	- Aqueous dispersion of the polymer of Example 4 (prepared according to Example 11.1)	82.3 g
	- Water	15 g
	- Glycerol	2 g
	- Formaldehyde	0.5 g
	- Hydroxypropyl cellulose	0.2 g

10

The aqueous dispersion, glycerol, and formaldehyde were mixed, following by gentle stirring; then the hydroxypropyl cellulose was dispersed in the resulting solution.

15

This composition is easy to apply to the nail, and yields a glossy film which is easily eliminated with water. After several weeks of application, daily application of this composition onto the nail results in hardening of the nails.

## CLAIMS

1. The use, in and for the preparation of cosmetic or dermatological compositions, of a copolymer capable of being produced by copolymerization of a mixture of monomers comprising:

(a) 5 to 25% by weight of at least one ethylene-unsaturated monomer (A) having at least one carboxylic acid group;

(b) 3 to 30% by weight of at least one monomer (B) having the formula (I):



in which

- $\text{R}_1$  designates a hydrogen atom or a methyl radical; and
- $\text{R}_2$  designates a linear, branched or cyclic, saturated, unsaturated or aromatic alkyl radical having 8 to 40 carbon atoms;

(c) at least one monomer (C) selected from the group constituted by tert-butyl methacrylate, tert-butyl acrylate, and their mixtures, in a proportion at least greater than 50% by weight, such that the glass transition temperature ( $T_g$ ) of the polymer is greater than or equal to 15°C;

the percentages by weight being calculated in terms of the total quantity of monomers used.

2. The use as defined in Claim 1, wherein the monomer or monomers (A) are selected from the group constituted by the ethylene-unsaturated carboxylic monoacids; the ethylene-unsaturated carboxylic diacids and their monoester or monoamide derivatives having one  $\text{C}_1 - \text{C}_4$  alkyl group; [and] allyloxyacetic acid.

3. The use as defined in one of Claims 1 or 2, wherein the monomer or monomers (B) [sic] are selected from the group constituted by acrylic acid, methacrylic acid, or mixtures thereof.

4. The use as defined in any one of Claims 1 through 3, wherein  $R_2$  is a linear or branched saturated alkyl radical having from 8 to 40 carbon atoms.

5. The use as defined in any one of the foregoing claims, wherein the copolymer comprises 6 to 20% by weight of monomer (A), 5 to 25% by weight of monomer (B), and 55% to 80% by weight of monomer (C).

6. The use as defined in any one of the foregoing claims, wherein the copolymer comprises 6 to 15% by weight of monomer (A), 13 to 22% by weight of monomer (B), and 60 to 70% by weight of monomer (C).

7. The use as defined in any one of the foregoing claims, wherein the polymer consists of a mixture of the monomers of [sic] monomers (A), (B), and (C).

8. The use as defined in any one of Claims 1 through 7, wherein the copolymer has a glass transition temperature ranging from 40°C to 90°C.

9. The use as defined in any one of the foregoing claims, wherein the copolymers have an average molecular weight, measured at the top of the peak by stearic exclusion chromatography, ranging from 5000 to 2,000,000.

10. The use as defined in any one of the foregoing claims, wherein the copolymer is neutralized to a level ranging from 30 to 100% by means of a base.

11. A cosmetic or dermatological composition, wherein it contains, in a cosmetically or dermatologically acceptable medium, at least one copolymer as defined by any one of Claims 1 through 10.

5 12. The composition as defined in Claim 11, wherein the copolymer concentration in the cosmetic or dermatological compositions is generally between 0.1 and 50%, and preferably between 1 and 30%, in terms of the total weight of the composition.

10 13. The composition as defined in Claim 11 or 12, wherein the cosmetically or dermatologically acceptable substrate is preferably constituted by water, by one or more cosmetically acceptable organic solvents, or by a mixture of water and one or more cosmetically or dermatologically acceptable organic solvents.

15 14. The composition as defined in Claim 13, wherein the cosmetically or dermatologically acceptable organic solvents are selected from among the C<sub>1</sub> - C<sub>4</sub> lower alcohols.

20 15. The composition as defined in any one of Claims 11 through 14, wherein the graft copolymer is dissolved or in dispersion in the substrate of the composition.

25 16. The composition as defined in any one of Claims 11 through 15, wherein it also contains a plasticizing agent.

30 17. The composition as defined in any one of Claims 11 through 16, wherein it contains conventional cosmetic additives selected from among the fats such as mineral, vegetable, animal, or synthetic oils; animal, fossil, vegetable, mineral, or synthetic waxes; organic solvents; thickening agents; softeners;



antifoaming agents; moisturizing agents; humectants; processing agents; antiperspirants; alkalizing agents; UV-A or UV-B or broad-spectrum solar filters; coloring agents; pigments; perfumes; plasticizers; preservatives; anionic, nonionic, or amphoteric organic polymers, and propellants.

5

18. The composition as defined in any one of Claims 11 through 17, wherein it is a hair-care composition.

10

19. The composition as defined in any one of Claims 11 through 17, wherein it is a makeup composition.

20. The composition as defined in any one of Claims 11 through 17, wherein it is a skin-care composition.

15

21. Use of a copolymer as defined in any one of Claims 1 through 10 as a film-forming agent, or as a film-forming agent additive, in and for the preparation of a cosmetic or dermatological composition.

20

22. A method for cosmetic treatment of keratinaceous materials, wherein it consists in applying onto the latter a composition such as that defined in any one of Claims 11 through 20.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/FR 97/01165

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 A61K7/06 A61K7/48

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 552 755 A (N.A. RANDEN) 12 November 1985 Table III : composition nr. 18 see claims 1-6; examples 1-18; table I	1-22
X	PATENT ABSTRACTS OF JAPAN vol. 96, no. 008, 30 August 1996 & JP 08 092046 A (SHISEIDO), 9 April 1996, cited in the application see abstract	1-4, 7-9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*G\* document member of the same patent family

Date of the actual completion of the international search

31 October 1997

Date of mailing of the international search report

11.11.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-2016

Authorized officer

Willekens, G

26

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/FR 97/01165

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4552755 A	12-11-85	NONE	

(27)